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Reversible and Resistant Components of PCB Adsorption-Desorption Adsorbent Concentration Effects

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16. ABSTRACT

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REVERSIBLE AND RESISTANT COMPONENTS OF PCB ADSORPTION-DESORPTION: ADSORBENT CONCENTRATION EFFECTS

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ABSTRACT. *Laboratory experiments and analysis of field data from Saginaw Bay show that the concentration of suspended adsorbent affects the partition coefficient of PCB. The coefficient consistently decreases as adsorbent concentration increases. In addition it has been found that adsorption and desorption are not completely reversible. An analysis of this effect is presented within the framework of the resistant-reversible component model of adsorption-desorption. The partition coefficients for these two components are found to behave quite regularly: the resistant component exhibits essentially constant partitioning whereas the reversible component partition coefficient is exactly inverse to adsorbent concentration. The interplay of these components determines the variation of the adsorption and desorption partition coefficients as functions of adsorbent concentration and the degree of reversibility to be expected. Saginaw Bay field data conform to the relationship derived from the resistant-reversible model.*

INTRODUCTION

The partitioning of hydrophobic chemicals between dissolved and particulate phases in aqueous environments is a mechanism of fundamental importance in determining the fate of these materials in the environment. The magnitude of this partitioning is, therefore, of substantial concern, and quantitative relationships are required in any rational assessment procedure. Methods for computing the fate of these chemicals all require a specification of the behavior of the adsorption and desorption reactions which transfer chemical between these phases (Baughman and Lassiter 1978, Thomann and Di Toro 1979). In order to provide these data for use in analysis of PCB distributions in Saginaw Bay, a series of experiments was conducted using Saginaw Bay sediments and various inorganic clays as adsorbents, and the 2,4,5,2',4',5' isomer, hexachlorobiphenyl (abbreviated as HCBP), as the adsorbate.

The experiments focused on two phenomena: the reversibility of adsorption and desorption; and the effect of adsorbent mass on the extent of partitioning. The latter effect is related to the well-known phenomenon that the fraction of adsorbate in the particulate phase increases as the mass of adsorbent increases. What is surprising is that, in some cases, the extent to which the particulate fraction increases is inconsistent with the conventional assumption that the isotherm parameters are independent of the concentration of adsorbent mass. In particular, some observations indicate that isotherm parameters are indeed influenced by the sediment concentration used for the adsorption experiment (Huang and Liao 1970, Lotse *et al.* 1968, Connolly 1980). For linear isotherms, for which the relevant parameter is the partition coefficient, π, it has been observed for many adsorbate-adsorbent pairs, (O'Connor and Connolly 1980) that the partition coefficient decreases systematically as adsorbent concentration, m, increases. This is an important observation with many practical implications.

A series of experiments has been performed which reproduces this effect for HCBP adsorption. Possible experimental artifacts which may explain the effect have also been investigated. It has been found (Horzempa and Di Toro 1982) that the effect is not caused by nonlinear isotherms improperly characterized by a single partition coefficient, or by unintended aqueous or particulate phase changes that result as a consequence of adsorbent concen-

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tration increases. The conclusion from these experiments is that the phenomenon is real and must be considered systematically in the description of HCBP adsorption and desorption.

The second focus of the experiments is the extent of reversibility of the adsorption reaction. As both adsorption and desorption are occurring in natural systems, the experiments were designed to address both processes. It was consistently found that the adsorption reaction was not completely reversible, and, depending upon the details of the experiment, a substantial quantity of adsorbed HCBP remained in the particulate phase after desorption, in excess of that which would be predicted by the adsorption isotherm.

This disturbing result implies that the conventional reversible description of adsorption-desorption is inadequate and that a refined quantitative desorption is required. It has been proposed (Di Toro and Horzempa 1982a) that the process can be consistently described if the adsorbed HCBP is assumed to be composed of two components: a reversible component which readily adsorbs and desorbs reversibly; and a resistant component which resists desorption during the single desorption phase of the experiment, and may or may not ultimately desorb during consecutive desorptions. The irreversibility has been found to persist under a variety of experimental modifications: it is not affected by either the time of desorption or the manner of phase separation, and it occurs for clay adsorbates as well as Saginaw Bay sediments (Horzempa and Di Toro 1982).

The dual focus of the experimental results presented in this paper makes it possible to investigate the effect of adsorbent concentration on both the reversible and resistant components of HCBP adsorption. It is shown below that the observed systematic variation of adsorption and single desorption partition coefficient as a function of sediment concentration can be explained in terms of the behavior of the reversible and resistant partition coefficients. The latter has been found to be approximately constant with respect to adsorbent concentration variations, as would be expected from conventional adsorption theory, whereas the reversible partition coefficient has been found to be inversely proportional to adsorbent concentration. The interplay of these two components determines the variation of the adsorption and single desorption partition coefficients as a function of adsorbent concentration. This finding provides insight into the possible mechanisms that are responsible for this puzzling behavior and it suggests that further experimental investigations of the absorbent dependency of partitioning be accompanied by desorption measurements to clarify the role of the reversible and resistant components.

It is the purpose of this paper to present the analysis of these experimental data and to relate these findings to the conventional descriptions of adsorption-desorption as applied to the computation of the fate of PCB in natural water systems.

DEFININTIONS AND METHODOLOGY

At adsorption equilibrium, let r_a and c_a be the particulate (ng/kg) and dissolved (ng/L) HCBP concentrations, respectively. The adsorption partition coefficient, π_a, (L/kg) is defined as the slope of the linear isotherm: $r_a = \pi_a c_a$. As the adsorbent solids are required for the desorption phase of the experiment, the particulate concentration is obtained from the difference between the total HCBP concentration in the adsorbent-aqueous phase mixture, c_{Ta}, and the aqueous phase concentration after centrifugation, c_a, i.e., $r_a = (c_{Ta} - c_a)/m_a$, where m_a is the concentration of adsorbent solids during the adsorption phase of the experiment.

Following centrifugation, the contaminated aqueous phase is replaced by uncontaminated aqueous phase, and at desorption equilibrium the total, c_{Td}, and dissolved, c_d, HCBP concentrations are measured. The particulate concentration, r_d, is again estimated by difference: $r_d = (C_{Td} - c_d)/m_d$. The single desorption partition coefficient, π_d, is defined as the slope of the desorption isotherm: $r_d = \pi_d c_d$.

For isotherm experiments at a fixed adsorbent concentration with many pairs of adsorption (r_a,c_a) and desorption (r_d,c_d) data, the adsorption and desorption partition coefficients are obtained as the slopes of r_a versus c_a and r_d versus c_d, respectively. For experiments that are designed to investigate the effect of adsorbent concentration variations, it is inconvenient to evaluate a complete isotherm at each adsorbent concentration of interest. Rather, the concentration of adsorbent is varied systematically. In order to reduce the effect of systematically varying aqueous concentrations—for example if a constant initial HCBP concentration is used, then the equilibrium dissolved concentration would decrease systematically as adsorbent concentration increases—the initial concentration is varied to produce similar equilibrium dissolved concentrations (Di Toro and Horzempa 1982b). The results of this experimental design are (triply replicated)

pairs of adsorption (c_a,r_a) and desorption (c_d,r_d) points at varying adsorbent concentrations, m. The partition coefficients are then calculated from the ratio r and c, i.e., $\pi_a = r_a/c_a$ and $\pi_d = r_d/c_d$.

For some of the initial experiments which were focused on desorption, the total HCBP concentration at adsorption equilibria, c_{Ta}, was not measured so that a direct estimate of r_a is not available. It has been found, however, that no significant vessel adsorption or desorption occurs during the desorption phase of the experiment so that the mass balance relationship:

$$m\, r_a = c_{Td} \tag{1}$$

can be used to estimate r_a. Figure 1 presents the experimental confirmation of this relationship for those experiments in which both r_a and c_{Td} are available. The histogram illustrates that the percent error, 100% $(m\, r_a - c_{Td})/c_{Td}$, is within ±7.5% for 72% of the observations. No significant bias is observed, which confirms the assumption that no significant vessel adsorption or desorption occurs during the desorption phase of the experiment.

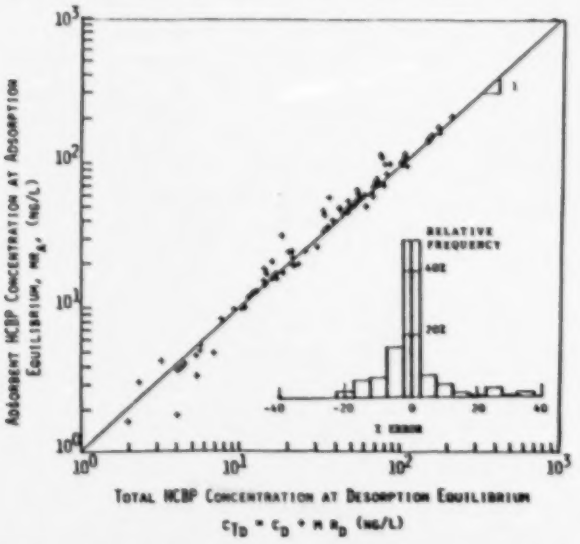

FIG. 1. Extent of vessel adsorption-desorption at desorption equilibrium.

The variations of the adsorption, π_a, and desorption, π_d, partition coefficients as a function of adsorbent concentration are shown in Figure 2. Two adsorbents, Saginaw Bay sediment (Station #50) and Montmorillonite, and two aqueous phases, distilled water and supernatant—which is distilled water previously equilibrated with uncontaminated adsorbent—are shown. The data points are averages of triplicate replicates, the curves are discussed below. The systematic decrease of both adsorption and single desorption partition coefficients as adsorbent concentration increases is apparent, as is the irreversibility of adsorption-desorption, illustrated by the fact that π_d exceeds π_a. It can be seen that the extent of irreversibility increases as adsorbent concentration increases. A more complete description of these experimental modifications employed to ensure that the results are not experimental artifacts is given elsewhere (Horzempa and Di Toro 1982).

The purpose of this paper is to analyze these results in terms of reversible and resistant component behavior. The definitions of these components are illustrated in Figure 3. The resistant particulate concentration: r_o, is estimated by a linear extrapolation of the adsorption, r_a, and single desorption, r_d, particulate concentration to zero dissolved concentration. It has been found (Di Toro and Horzempa 1982a) that a linear isotherm governs the extent of resistant adsorption: $r_o = \pi_o c_a$ which defines the resistant partition coefficient, π_o. Further the reversible component concentration at both adsorption, $r_{xa} = r_a - r_o$, and single desorption, $r_{xd} = r_d - r_o$, equilibria are both described by a linear isotherm with the same partition coefficient, π_x. That is: $r_{xa} = \pi_x c_a$ and $r_{xd} = \pi_x c_d$, for all the pairs of experimental points on the isotherm.

From the geometry of the relationships in Figure 3 it is clear that the partition coefficients for the reversible and resistant components are given by:

$$\pi_x = \frac{r_a - r_d}{c_a - c_d} \tag{2}$$

and

$$\pi_o = \frac{r_a}{c_a} - \frac{r_a - r_d}{c_a - c_d} \tag{3}$$

The second equation follows from the fact that $\pi_a = \pi_o + \pi_x$. This completes the discussion of the methodology and definitions to be employed subsequently in the analysis of the experimental data.

ADSORBENT MASS EFFECTS FOR REVERSIBLE AND RESISTANT PARTITION COEFFICIENTS

The results of these experiments analyzed in terms of reversible and resistant partition coefficients,

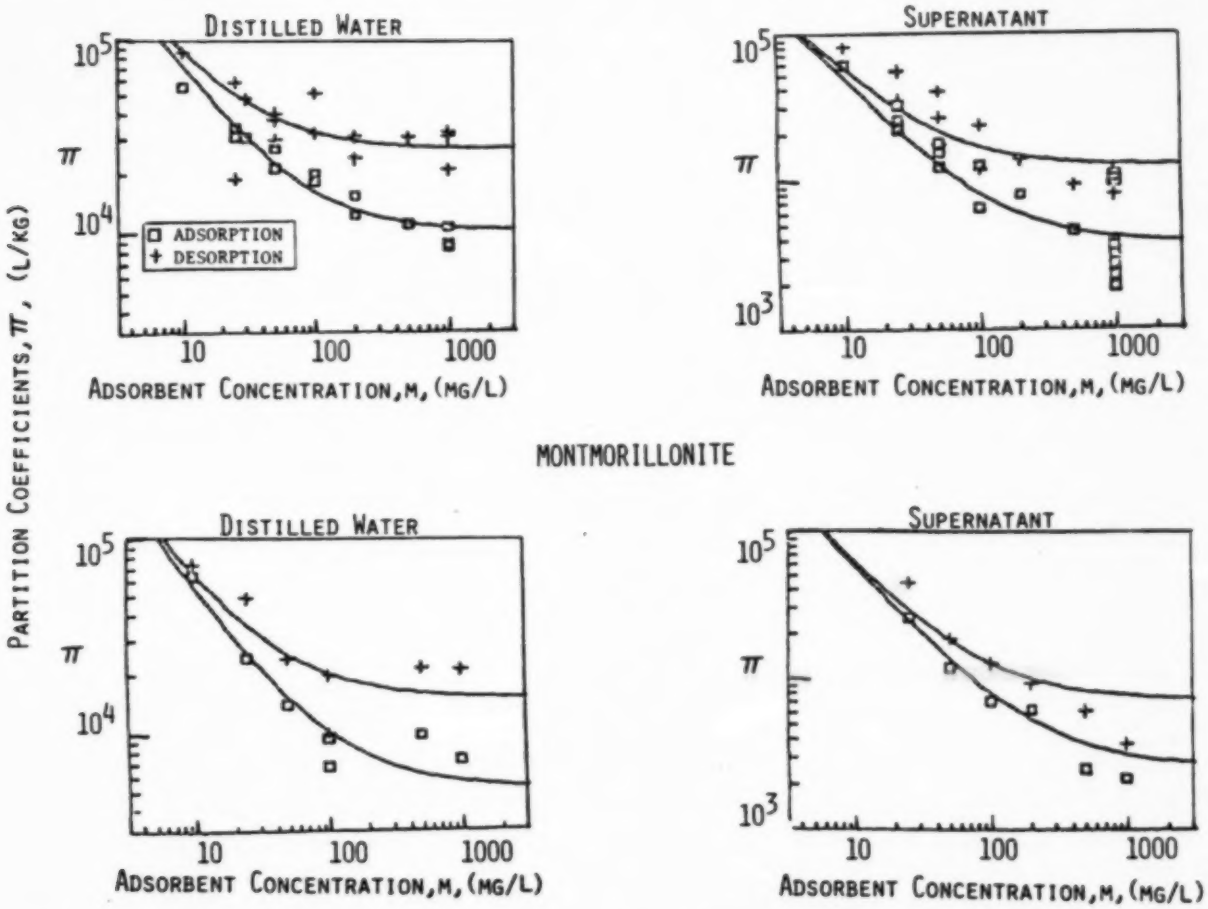

FIG. 2. Adsorption and desorption partition coefficient variation with adsorbent concentration. Saginaw Bay Station #50 and montmorillonite. Distilled water and supernatant aqueous phases. Curves are Equation 7 for adsorption and Equation 8 for desorption partition coefficient.

Equation 2 and Equation 3, are shown in Figure 4 for Saginaw Bay sediment (Station #50) and Figure 5 for Montmorillonite. They correspond to the adsorption-desorption data presented in Figure 2. The open squares represent triplicate logarithmic averages of the partition coefficients. The filled circles are the logarithmic average ± the standard error of the average from isotherm experiments, each of which was conducted at the fixed adsorbent concentrations as indicated in the figure. (These isotherms were only available for distilled water as the aqueous phase.)

For the Saginaw Bay sediment, Figure 4, it is found that the resistant component partition coefficient, π_o, is independent of adsorbent concentration whereas the reversible component partition coefficient, π_x, is inversely proportional to adsorbent concentration. The lines on the plot have slopes of zero and minus one respectively. For montmorillonite, Figure 5, the resistant component coefficient appears to decrease slightly for distilled water and more markedly for supernatant as the aqueous phase. However, the reversible component partition coefficients are both inversely proportional to mass as was the case for Saginaw Bay sediment.

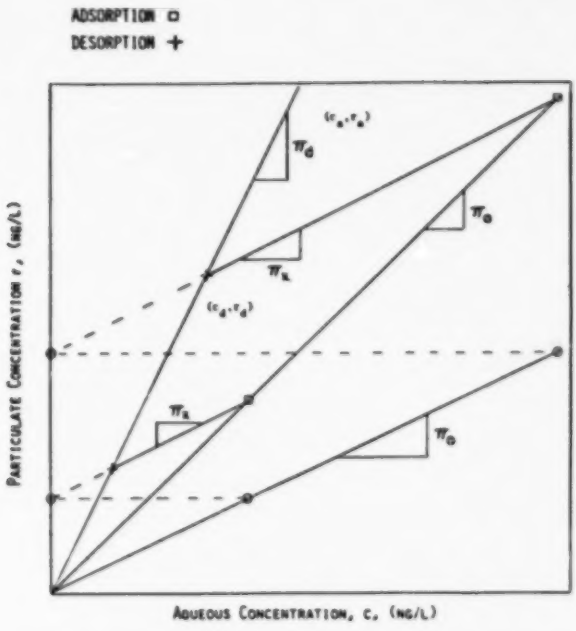

FIG. 3. Definition of adsorption, π_a; desorption, π_d; reversible, π_x; and resistant, π_o partition coefficients.

Regression analyses of these data, using the relationship: $\pi = am^n$ (O'Connor and Connolly 1980), are given in Table 1. The slopes, n, for the reversible component partition coefficient relationship are all found to be n = -1 within 95% confidence limits. This inverse relationship between π_x and m, i.e.:

$$\pi_x = \nu_x m^{-1} \tag{4}$$

defines ν_x, a dimensionless distribution coefficient for the reversible component. However, for the resistant component partition coefficients, only the Saginaw Bay sediment yields n = o within the confidence limits. Nevertheless, it is a useful approximation to assume that the resistant component partition coefficient, π_o, is constant with respect to adsorbent concentration, m. Hence a consistent description of the reversible and resistant component partition coefficient—adsorbent concentration relationships requires two parameters only: a resistant component partition coefficient: π_o and a reversible component distribution coefficient: ν_x.

The utility of this assumption is that it provides a concise description of the behavior of the variation of adsorption, π_a, and desorption, π_d, partition coefficients as functions of adsorbent concentration. This can be shown as follows. For π_x, it follows from Equation 2 that:

$$\pi_x = \frac{\pi_a - \pi_d(c_d/c_a)}{1 + (c_d/c_a)} \tag{5}$$

The relationship between c_a and c_d follows from the mass balance relationship: Equation 1, and the fact that $c_{Td} = c_d + m\, r_d$ so that:

$$\frac{c_d}{c_a} = \frac{m\pi_a}{1 + m\pi_d} \tag{6}$$

Using these equations, solving for π_a and π_d in terms of π_o and π_x, and using Equation 4 for π_x yields:

$$\pi_a = \pi_o = \frac{\nu_x}{m} \tag{7}$$

$$\pi_d = \pi_o\left(1 + \frac{1}{\nu_x}\right) + \frac{\nu_x}{m} \tag{8}$$

The curves in Figure 2 for π_a and π_d versus m are these relationships using constant π_o and ν_x represented by lines in Figures 4 and 5, and the average values given in Table 1. The extent of the goodness of fit reflects the assumption of constant π_o: the fit is better for Saginaw Bay sediment than for montmorillonite, as is expected, as the assumption of constant π_o is more appropriate for the former data.

EFFECT OF ADSORBENT CHARACTERISTICS

It has been proposed in the previous section that the adsorption and desorption behavior of HCBP can be described in terms of two parameters, π_o and ν_x, which are essentially independent of the adsorbent concentration. However, they may be functions of the types of adsorbent used. To investigate these relationships, a series of experiments was conducted using various samples of Saginaw Bay sediment. The descriptions of the sampling locations and the bulk physical and chemical properties of the samples are reported elsewhere (Di Toro and Horzempa 1982b). These samples were wet seived ($<100\mu$) to remove the sediment material that would be unlikely to be resuspended or contribute an appreciable fraction of adsorbing surface area. An exception to this procedure was Station #69 which was found to contain

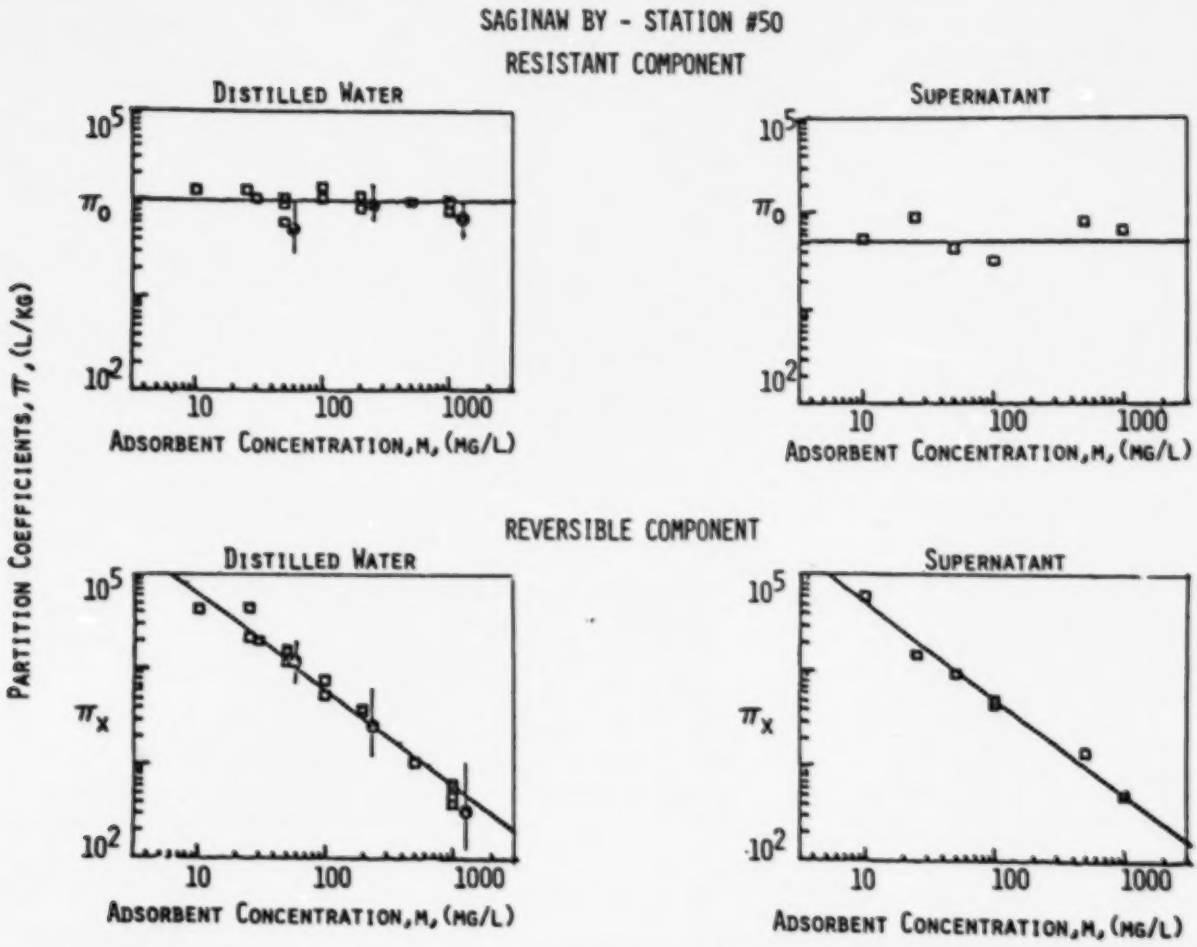

FIG. 4. Resistant and reversible component partition coefficient variation with adsorbent concentration Saginaw Bay Station #50. Distilled water and supernatant as aqueous phase.

mostly sandy sediment. For this station the procedure was reversed and the larger fraction (>100μ) was retained, in order that one sample of coarse sediment is included in the experiments. Montmorillonite is included as a purely inorganic sediment.

The results of the adsorption-desorption isotherm experiments are shown in Figure 6. The straight lines are linear isotherms for the average adsorption and desorption partition coefficients, which are listed in Table 2. Although there is some tendency for the desorption isotherm to be nonlinear, the fits are reasonable representations of the data. Nonreversible behavior is found in all cases, but is quite small for Station #69 in contrast to the other stations. Note that the Station #69 particulate HCBP concentrations are an order of magnitude smaller and the dissolved HCBP concentrations are an order of magnitude larger than the other stations. In addition, the adsorbent concentration used for this isotherm is much larger (m = 20,000 mg/L) than for the rest of the adsorbents (m = 1100 mg/L). This was necessary in order that appreciable particulate HCBP concentrations resulted. Nevertheless, as shown subsequently, the results for this sediment are in conformity with the model proposed in this paper.

The variation in adsorption partition coefficient has been correlated to organic carbon content of the sediment (Karickhoff *et al.* 1979) and to the sediment surface area (Hiraizumi *et al.* 1979). As suggested above, the most concise description of

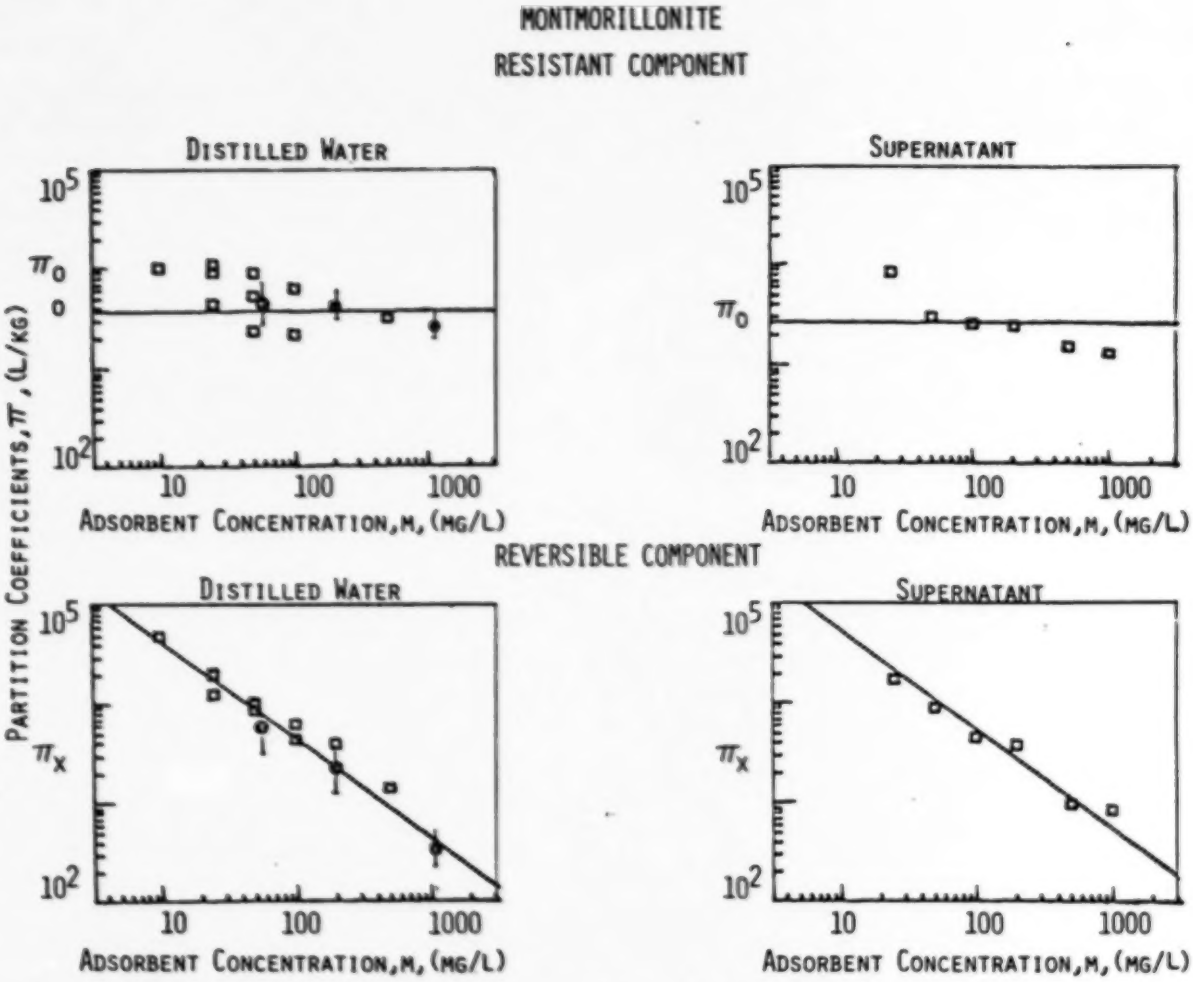

FIG. 5. Resistant and reversible component partition coefficient variation with adsorbent concentration. Montmorillonite. Distilled water and supernatant as aqueous phase.

adsorption and desorption is in terms of the resistant component partition coefficient, π_o, and the reversible component distribution coefficient, ν_x. The variation of these coefficients (mean ± standard deviation) as functions of percent volatile solids (% VSS) and specific surface area (σ) as determined by a single point N_2-BET isotherm, are shown in Figure 7. The variation of the resistant component partition coefficient, π_o, with % VSS (Figure 7a) is fairly regular for the Saginaw Bay stations, but montmorillonite does not conform to the relationship since it has a significant π_o and no volatile solids fraction. The surface area correlation (Figure 7b) is more erratic and again montmorillonite does not conform.

The variation of the reversible component distribution coefficient, ν_x, with volatile solids fraction (Figure 7c) and surface area (Figure 7d) is not systematic, although there is a slight trend for ν_x to increase with volatile solids fraction. The surprising result is that to within approximately a factor of three the reversible component distribution coefficient is nearly constant and independent of sediment properties. The value obtained for the coarse fraction ($>100\mu$) of Station #69 sediment (ν_x = 0.545) is consistent with the range for the fine fraction ($<100\mu$) of the other Saginaw Bay stations (ν_x = 0.496 - 1.18) and for montmorillonite (ν_x = 0.349). This weak variation of the reversible component distribution coefficient as a function of

TABLE 1. Regression analyses of adsorbent concentration effect.

Adsorbent	Aqueous Phase	Resistant Component Partition Coefficient*			Reversible Component Partition Coefficient*		
		π_o(L/kg) Slope	π_o(L/kg) Intercept ($\times 10^{-3}$)	Average π_o(L/g)	π_x(L/kg) Slope	π_x(L/kg) Intercept ($\times 10^{-6}$)	Average ν_x
Saginaw Bay Station #50	Distilled Water	-0.015 (0.039, -0.070)	9.64 (12.6, 7.33)	10.0	-1.025 (-0.98, -1.07)	0.681 (.862, .538)	0.624
Saginaw Bay Station #50	Supernatant	0.011 (0.093, -0.07)	5.83 (8.72, 3.90)	5.29	-0.952 (-0.90, -1.01)	.410 (.534, .315)	0.521
Montmorillonite	Distilled Water	-0.247 (-0.21, -0.29)	13.6 (16.9, 10.9)	3.62	-1.04 (-1.01, -1.06)	.541 (.635, .461)	0.439
Montmorillonite	Supernatant	-0.421 (-0.35, 0.49)	2.12 (3.09, 1.45)	2.61	-0.855 (-0.79, -0.92)	.261 (.367, 1.86)	0.557

*Values in parentheses are regression coefficients ± standard errors of the estimates.

adsorbent properties contrasts sharply with the strong variation of the resistant component partition coefficient: whereas the range of ν_x is 0.349–1.18, the range of π_o is 0.009–14.0 (L/g).

A multiple linear regression analysis of these data, shown in Table 3, further illustrates this result. Whereas the regression equation for π_o has a small constant term relative to the contribution of the volatile solids fraction and surface area, the reverse is true for ν_x. The observed resistant component partition coefficients are well represented by the linear relationship (Table 3), as indicated by the large fraction of the variance removed by the regression ($R^2 = 0.953$), whereas the reversible component distribution coefficient is less well represented, although a significant fraction of the variance is removed by the regression ($R^2 = 0.66$). In fact, the regression equation is not a dramatic improvement over the assumption of a constant ν_x. Further experimental information is required in order to refine these relationships for ν_x, if indeed they exist.

IMPLICATIONS FOR MODELING PCB FATE IN NATURAL WATERS

The results of these experiments and their analysis in terms of a resistant partition coefficient and a reversible component distribution coefficient directly impact the formulations used to model the fate of chemicals which adsorb to suspended and sedimented particles. The conventional assumptions are that the adsorption-desorption reaction is reversible and, for a linear isotherm relationship, that the partition coefficients are constant with respect to adsorbent concentration. Both of these assumptions have been shown to be inappropriate approximations of the experimentally observed behavior of HCBP.

The issue of the impact of the resistant component on the eventual fate of HCBP is still uncertain as it has been shown that apparently this component does eventually desorb at very low aqueous concentration (Horzempa and Di Toro 1982). Whether the desorption is complete is uncertain at present. A more detailed investigation of this phenomenon is underway at present.

The adsorbent concentration effects, however, can have a substantial impact on the computation of the fate of PCB. The transport processes and kinetic reactions are significantly different for adsorbed (= particulate) and dissolved chemical fractions. These are estimated using the relationships:

$$f_d = \frac{1}{1 + m\pi_a} \tag{9}$$

$$f_p = \frac{m\pi_a}{1 + m\pi_a} \tag{10}$$

where $f_d = c_a/c_{Ta}$ and $f_p = 1 - f_d$. These equations follow directly from the mass balance equation $c_{Ta} = c_a + mr_a$, and the linear isotherm: $r_a = \pi_a c_a$. A useful quantity is the ratio of particulate to dissolved fraction:

$$\frac{f_p}{f_d} = m\,\pi_a \tag{11}$$

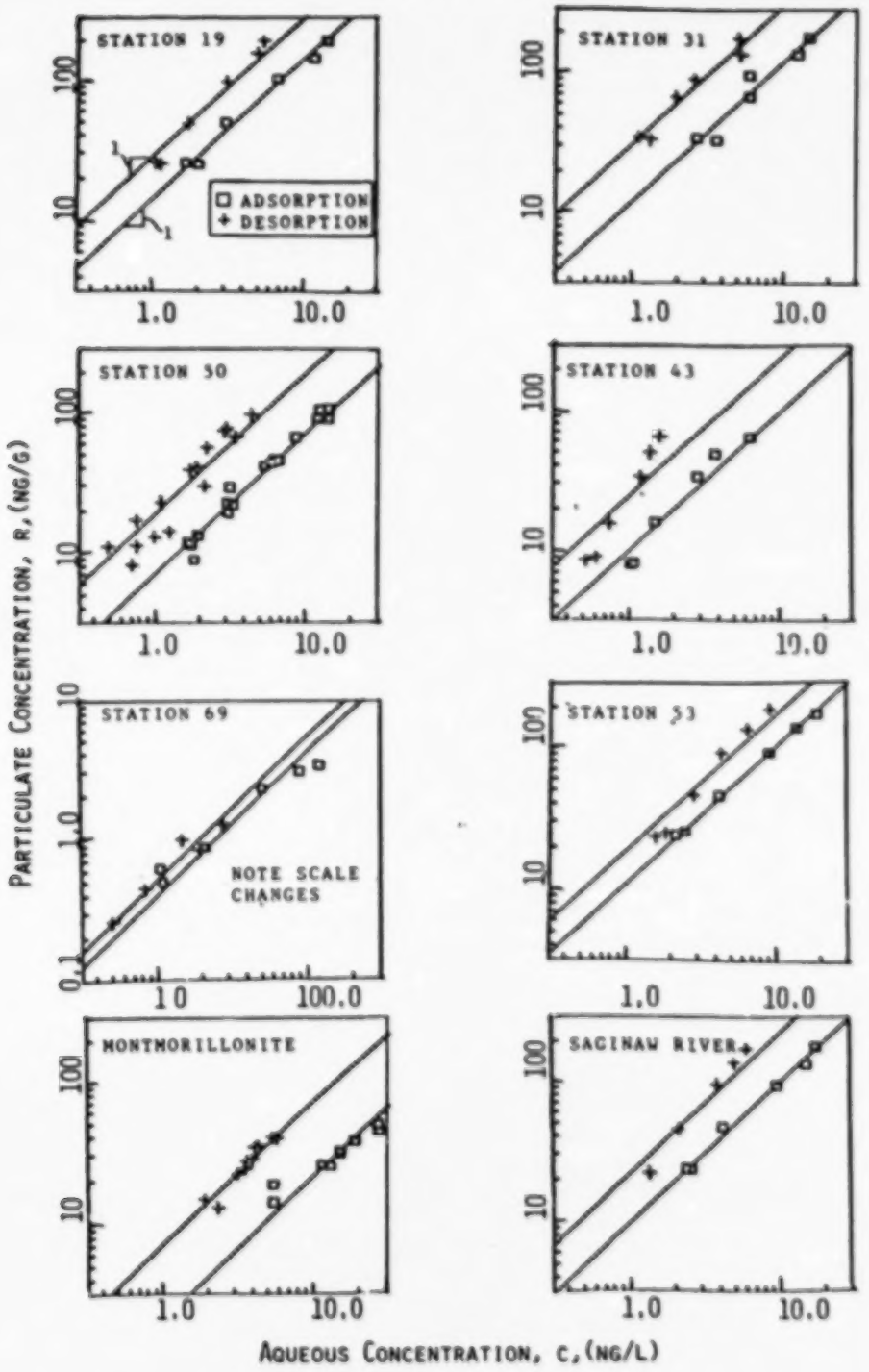

FIG. 6. Adsorption and desorption isotherms for Saginaw Bay stations and montmorillonite.

*TABLE 2. Experimental data for partition coefficients.**

Sediment	Volatile Solids (%)	Specific Area (m^2/g)	Adsorbent Concentration (mg/L)	Adsorption π_a (L/g)	Desorption π_d (L/g)	Resistant π_o (L/g)	Reversible** ν_x
Saginaw Bay							
19	15	17	1,100	14.8 (15)	30.1 (18)	14.0 (14)	0.915 (44)
31	9.9	17.8	1,100	12.3 (18)	30.9 (17)	11.7 (18)	0.630 (39)
43	9.3	15.9	1,100	10.7 (21)	26.1 (35)	10.1 (21)	0.653 (66)
50	7.6	12.8	1,100	7.01 (17)	20.2 (32)	6.56 (17)	0.496 (52)
53	8.7	7.0	1,100	11.2 (7)	19.8 (22)	10.1 (8)	1.18 (48)
69	0.3	0.2	22,000	0.036 (27)	0.052 (25)	0.0087 (64)	0.545 (46)
Saginaw River	9.6	8.4	1,100	9.63 (12)	22.4 (23)	8.99 (12)	0.702 (43)
Montmorillonite	0.0	12.6	1,100	2.10 (17)	7.23 (15)	1.79 (16)	0.349 (29)

*The numbers in parentheses are the standard errors of the experimental data, in percent.
**This is the unitless distribution coefficient: $\nu_x = \pi_x m^{-1}$.

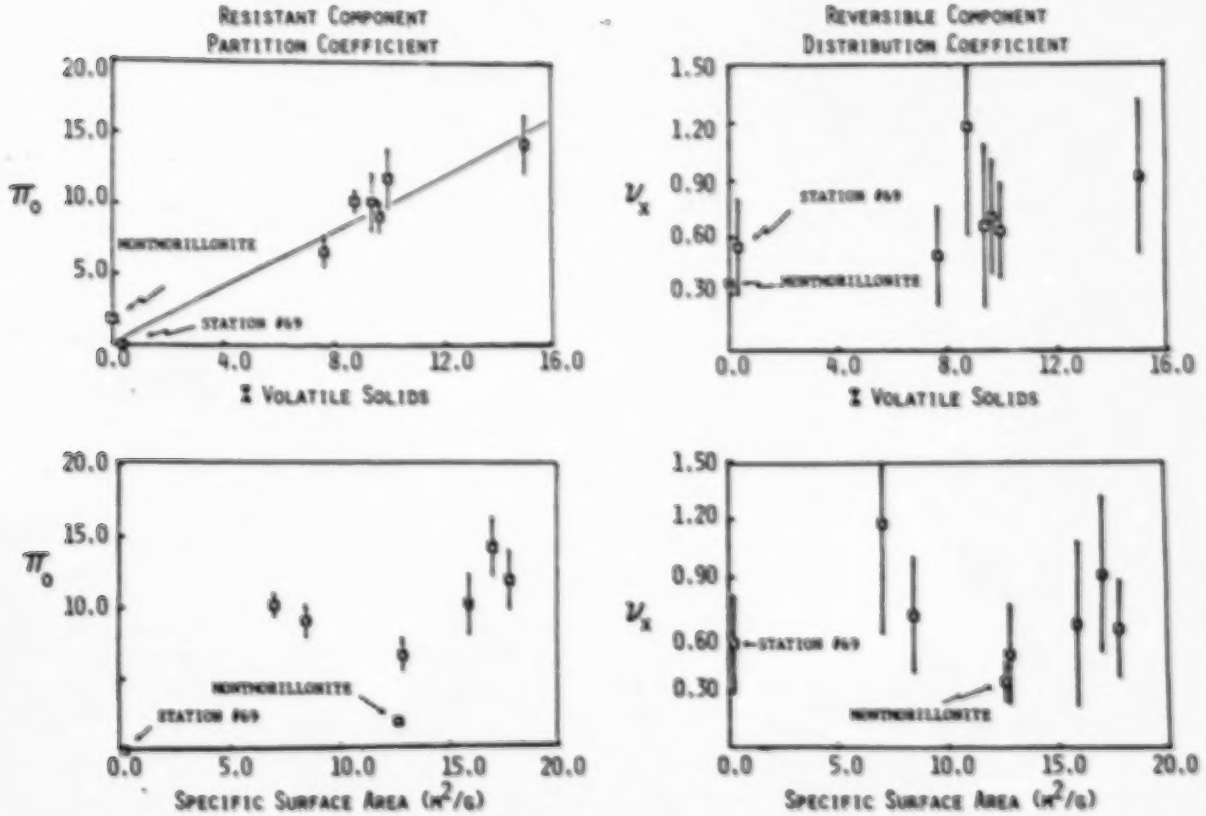

FIG. 7. Variation of resistant component partition coefficient and reversible component distribution coefficient with respect to percent volatile solids and specific surface area.

TABLE 3. Multiple linear regression analysis.*

	Constant	Volatile Solids** VSS(%)	Surface Area** $\sigma(m^2/g)$	Multiple Regression Coefficient R^2
π_o(L/g)	0.219	0.850 (0.115)	0.110(0.097)	0.953
ν_x	0.625	0.0507(0.0163)	-0.028(0.0138)	0.660

*Prediction Equations are:

$\pi_o = 0.219 + 0.850\ (\%\ VSS) + 0.110\ \sigma$
$\nu_x = 0.625 + 0.0507\ (\%\ VSS) - 0.028\ \sigma$

**The numbers in parentheses are the estimated standard errors of the coefficients.

since if the adsorption partition coefficient is independent of the adsorbent concentration, m, then one would expect that a graph of f_p/f_d versus m would be a straight line.

It has been shown above, however, that π_a is indeed a function of m and that Equation 7 provides an expression of this variation. The result is that the ratio of particulate to dissolved fraction should vary as:

$$\frac{f_p}{f_d} = \nu_x + m\pi_o \qquad (12)$$

where ν_x and π_o are constant with respect to m. Thus, at low suspended solids concentrations, the particulate fraction should approach ν_x following Equation 12 and not approach zero, as implied by Equation 11.

The experimental adsorption data, presented in this way, are shown in Figure 8. The straight line is Equation 11 using $\pi_a = \pi_o$, the curved line is Equation 12 with $\nu_x = 0.5$ for all cases and π_o as indicated. The marked deviation from straight line behavior is a consequence of the adsorbent concentration dependent adsorption partition coefficient. The data for quartz and kaolinite as adsorbents also appear to conform to this relationship, as shown in Figure 8.

These data are all laboratory experimental results. The fact that ν_x is approximately independent of adsorbent properties, however, suggests that field data would also exhibit the same solids dependency if π_o is not fluctuating too widely. Figure 9 illustrates the relationship for $\log_{10} f_p/f_d$ versus m for Saginaw Bay suspended particulates. The line is a linear regression. Using Equation 12 for the particulate to dissolved ratio, and the approximation: Ln $(1 + \epsilon) \simeq \epsilon$ for ϵ small yields:

$$\log_{10}(\nu_x + m\ \pi_o) \simeq \frac{1}{2.303}(\text{Ln}\ \nu_x + m\ \pi_o/\nu_x) \qquad (13)$$

The regression slope (0.0343 L/mg) and intercept (-0.532) yields $\nu_x = 0.294$ and $\pi = 23.2$ L/g. The reversible component distribution coefficient is at the lower range of the experimental values (ν_x = 0.35 - 1.2) and the resistant component partition coefficient is larger than those observed experimentally (π_o = 0.009 - 14.0 L/g). The latter result suggests that the percent volatile solids of the suspended particulates in Saginaw Bay is on the order of 20% (see Figure 7a) which is not unreasonable as a substantial fraction of the suspended particulate fraction is phytoplankton and detrital organic matter. Thus it appears that the Saginaw Bay suspended particulate PCB field data are in reasonable conformity with the experimental results, and, in particular, exhibit the relationship implied by the reversible-resistant model of PCB partitioning.

The implication of these results is that the expressions for dissolved and particulate fractions should be modified. In particular, the particulate fraction, Equation 10, becomes:

$$f_p = \frac{\nu_x + m\pi_o}{1 + \nu_x + m\pi_o} \qquad (14)$$

A comparison of this equation to the conventional expression (Equation 10) is shown in Figure 10. Whereas at adsorbent concentrations of less than 10 mg/L the conventional expression predicts no significant particulate fraction in the water column (f_p = 0.09), the revised expression, Equation 14 predicts a substantial particulate fraction (f_p = 0.38). Although this may be compensated for in numerical computation, by suitably increasing the "apparent" partition coefficient, the shapes of the two curves are quite different. The influence of this modification on detailed PCB fate calculations in Saginaw Bay is currently under way.

DISCUSSION AND CONCLUSIONS

The data presented for HCBP adsorption and desorption for various Saginaw Bay sediments and clay adsorbents clearly indicate that adsorbent concentration has a significant effect on the extent of partitioning. The behavior of the particulate fraction is quite different from that which is expected if π_a is constant.

The behavior of both the adsorption, π_a, and single desorption, π_d, partition coefficients as a function of adsorbent concentration is somewhat complicated. They are nearly equal at low adsor-

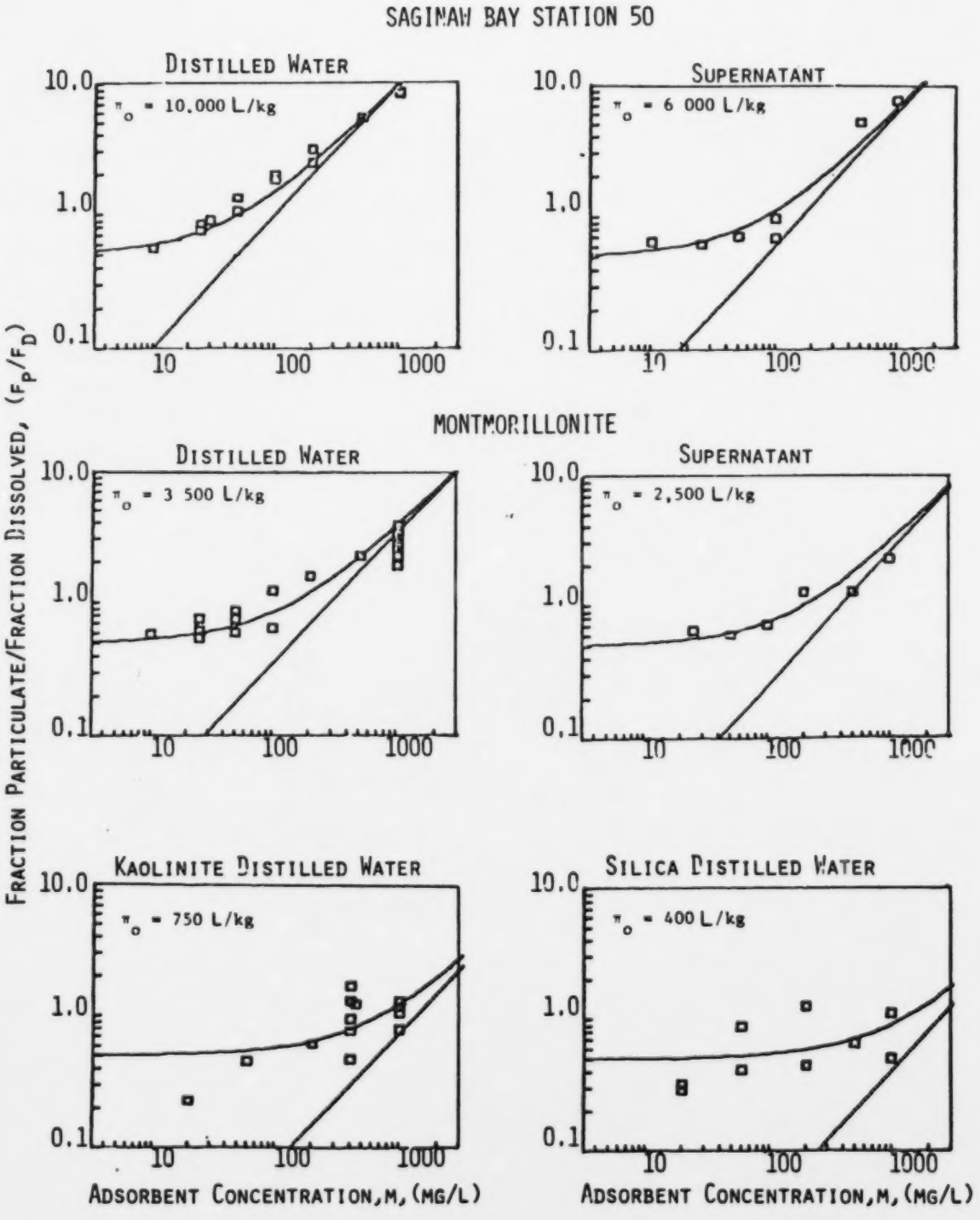

FIG. 8. Ratio of particulate to dissolved fraction of HCBP versus sediment concentration. Curves are Equation 12 evaluated with π_o as indicated and $\nu_x = 0.5$ for all cases. Straight lines are Equation 11 evaluated with $\pi_e = \pi_o$

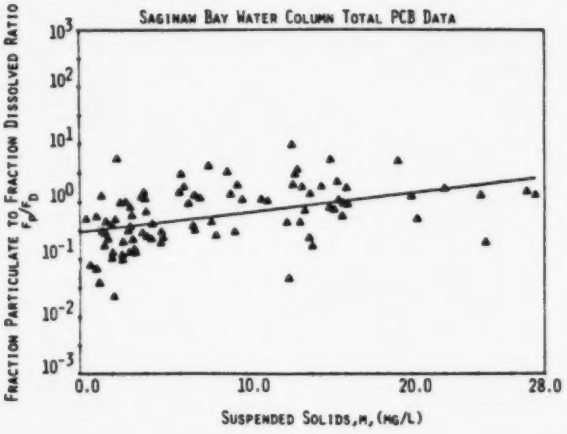

FIG. 9. Ratio of particulate to dissolved fraction of total PCB versus suspended solids concentration for Saginaw Bay. All cruises. Line is regression equation: $\log_{10} f_p/f_d = a + bm$; $a = -0.532$; $b = 0.0343$.

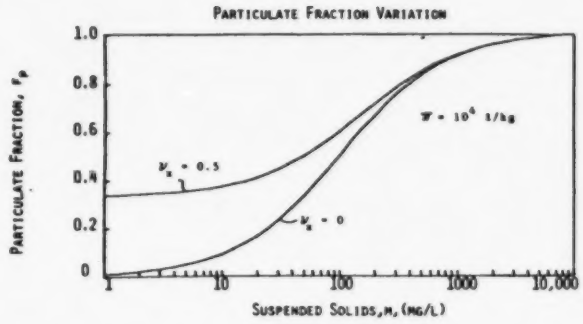

FIG. 10. Particulate fraction versus adsorbent concentration with and without adsorbent dependent partitioning.

bent concentrations (m = 10 mg/L) and both decrease as m increases. They appear to reach asymptotic values in the range of m = 200 – 1,000 mg/L. However, the desorption partition coefficient varies less markedly than the adsorption partition coefficient (Figure 2).

In contrast, the behavior of the partition coefficients for the reversible and resistant components is quite regular. The former is inversely proportional to adsorbent concentration and the parameter describing this behavior, ν_x, is found to be nearly a constant regardless of adsorbent type or properties. This is a remarkable result and suggests that some ubiquitous mechanism is the cause for the behavior of the exchangeable component.

In contrast, the resistant component partition coefficient has been found to be constant with respect to adsorbent concentration but to vary markedly with adsorbent type. The interplay of these two parameters determines the extent of the adsorbent concentration effect and the degree of reversibility observed, i.e., the extent to which $\pi_d \cong \pi_a$. Equations 7 and 8 specify the relationships. In particular, if the ratio of π_d to π_a is used as the measure of irreversibility, then they predict that:

$$\frac{\pi_d}{\pi_a} = \frac{m\pi_o\left(1 + \frac{1}{\nu_x}\right) + \nu_x}{m\pi_o + \nu_x} \qquad (15)$$

so that:

$$\frac{\pi_d}{\pi_a} \to \frac{1 + \nu_x}{\nu_x} \quad \text{as } m\pi_o \to \infty \qquad (16)$$

and

$$\frac{\pi_d}{\pi_a} \to 1 \quad \text{as } m\pi_o \to o \qquad (17)$$

Hence PCB adsorption-desorption should appear to be quite reversible at low values of $m\pi_o$ and to exhibit nonreversible characteristics, ($\pi_d/\pi_a \to 3$), at high values of $m\pi_o$.

This result explains the observed increase of nonreversible behavior as absorbent mass increases (Figure 2), and it also gives the quantitative explanation for the almost reversible behavior of the coarse Station #69 sediment (Figure 6). In spite of the fact that this isotherm was measured at a high sediment concentration, m = 20,000 mg/L, the resistant component partition coefficient for this sediment, $\pi_o = 0.0087$ L/g, is small so that $m\pi_d = 0.17$ is also small and $\pi_d/\pi_a = 1.44$ which indicates nearly reversible behavior.

The description of HCBP adsorbent concentration effects for both adsorption and desorption based upon resistant and reversible component behavior is certainly parsimonious and empirically quite successful. The difficulty that remains is to ascribe the results to mechanistic models. Partition coefficients that decrease as adsorbent concentration increases suggest that particle-particle interactions are responsible. But why should the variation be exactly inverse to mass and for the reversible component, and why should ν_x be independent of adsorbent type? Conversely, the resistant compo-

nent partition coefficient appears to be constant with respect to adsorbent mass, but a strong function of sediment type. The mechanism that accounts for this behavior is also unknown at present. Thus, although the description of adsorbent concentration effects in terms of the resistant and reversible component model is successful, it is not yet complete and additional experimental and theoretical investigations are required to determine what mechanisms are responsible for this regular, if puzzling, behavior of the components.

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